# SYNTHESIS AND CHARACTERIZATION OF BaTiO3 POWDER PREPARED BY COMBUSTION SYNTHESIS PROCESS

A THESIS SUBMITTED IN PARTIAL FULFILMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

**Bachelor of Technology**
**in**
**Ceramic Engineering**

By
**ANUJ KUMAR RAY**


Department of Ceramic Engineering
National Institute of Technology
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Under the Guidance of
**Dr. S. K. PRATIHAR**


**Department of Ceramic Engineering**
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# CERTIFICATE

This is to certify that the thesis entitled, "**SYNTHESIS AND CHARACTERIZATION OF BATiO3 POWDER PREPARED BY COMBUSTION SYNTHESIS PROCESS**" submitted by Sri **ANUJ KUMAR RAY** in partial fulfillment of the requirements of the award of Bachelor of Technology Degree in Ceramic Engineering at the National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other university / institute for the award of any Degree or Diploma.

Date:02.05.07

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Date: 02.04.07 ANUJ KUMAR RAY

***Contents***

# Abstract

The rapid growth of the electronic component industry has led to a demand for miniatured multilayer ceramic capacitor (MLCC), where $BaTiO_3$ is used due to its superior frequency characteristics, higher reliability, high breakdown voltage, excellent volumetric efficiency of the capacitance and reduced cost . MLCCs with a dielectric thickness of 2 μm have already been commercialized but the next generation components demand a thickness of 1 μm. Such requirement demands dielectric powders with uniform composition and size distribution, and weak agglomeration to allow low temperature sintering with minimum grain growth. Various methods of preparation of $BaTiO_3$ is available in the literature. The solid state route needs high calcinations temperature to get perovskite phase and often results in the formation of multiphase and inhomogeneous powders .High energy ball milling is also reported to produce 10nm particle size but the approach suffers from small batch size, high processing time and energy consumption. The complex double metal salts methods involve the use of solid precursors for the manufacture of pure $BaTiO_3$. The process suffers from the use of costly materials, multisteps, uncontrolled particle size and interparticle agglomeration. But A simple soft chemical method of synthesizing barium titanate nanopowders is described here, which is simple and cost effective , where titanium dioxide/titanium isopropoxide was taken as a source of titanium, and tartaric acid was taken as a template material, nitric acid as an oxidizing agent. The synthesized powders then characterized by XRD, TG and DTA, SEM spectroscopy. In this process phase pure barium titanate nanopowders can be prepared at a temperature of 900 °C.

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# Chapter 1

## GENERAL INTRODUCTION

## 1.1 Introduction

Barium titanate is an oxide of barium and titanium with the chemical formula $BaTiO_3$. It is a ferroelectric ceramic material, with a photorefractive effect and piezoelectric properties. It has five phases as a solid, listing from high temperature to low temperature: hexagonal, cubic, tetragonal, orthorhombic, and rhombohedral crystalstructure . All of the structures exhibit the ferroelectric effect except cubic.It has the appearance of a white powder or transparent crystals. It is insoluble in water and soluble in concentrated sulfuric acid.

Barium titanate can be manufactured by many sintering processes and optionally can be doped with different materials . Barium titanate is used as a dielectric material for ceramic capacitors, and as a piezoelectric material for microphones and other transducers. As a piezoelectric material, it was largely replaced by lead zirconate titanate, also known as PZT.

Polycrystalline barium titanate displays positive temperature coefficient, making it an useful material for thermistors and self-regulating electric heating systems

## 1.2 Properties of $BaTiO_3$

The chemical formula for Barium Titanate is $BaTiO_3$. As a powder it is white to grey in colour and has a perovskite structure. It is soluble in many acids including sulfuric, hydrochloric and hydrofluoric acids. It is insoluble in alkalis and water. In the pure form it is an electrical insulator. However, when doped with small amounts of metals, most notably scandium, yttrium, neodymium, samarium etc it becomes semiconducting. As a semiconductor it exhibits positive temperature of co-efficient of resistivity (PTCR) properties in the polycrystalline form. This means at a certain temperature, called the Curie temperature, the material will exhibit an increase in resistivity, the increase typically being several orders of magnitude. The Curie temperature can to some extent be controlled by the dopant. At the Curie temperature, barium titanate undergoes a phase

change from tetrahedral to cubic. It has also been reported that single crystals of barium titanate exhibit negative temperature co-efficient of resistivity (NTCR) properties. Barium titanate also exhibits ferroelectric properties and is an excellent photorefractive material.

Table-1(Key properties of $BaTiO_3$)

| Property | Value |
|---|---|
| Density ( $g.cm^{-3}$ ) | 6.02 |
| Melting Point (°C) | 1650 |
| Young's Modulus (GPa) | 67 |
| Hardness (Mohs) | 5 |

### 1.3 Mechanical property changes of $BaTiO_3$

Since barium titanate ($BaTiO_3$) can be made piezoelectric, it may be used to substitute hard tissues directly. As a first step in testing this concept, a series of in vivo and in vitro aging and biocompatibility studies were performed. The mean compressive strength of samples implanted subcutaneously in the backs of rabbits decreased to 138 MPa after 20 weeks from a control value of 281 MPa. Similar, though less drastic losses of strength were seen when specimens were aged in distilled water (182 MPa at 28 weeks) and Ringer's solution (159 MPa at 28 weeks). The most rapid decrease of strength in all cases was seen prior to 4 weeks. Thereafter, the decrease was much slower. Histological evaluation of the tissue surrounding the implant revealed a thin fibrous capsule and no evidence of tissue inflammation.

### 1.4 Dielectric Properties of $BaTiO_3$

Barium Titanate was the first developed piezoelectric ceramic and even now it is still widely used. It is also a well-known material used for capacitors. The crystallographic dimensions of the barium titanate lattice change with temperature, as shown in Figure 1.1,due to distortion of the $TiO_6$ octahedra as the temperature is lowered from the high temperature cubic form.

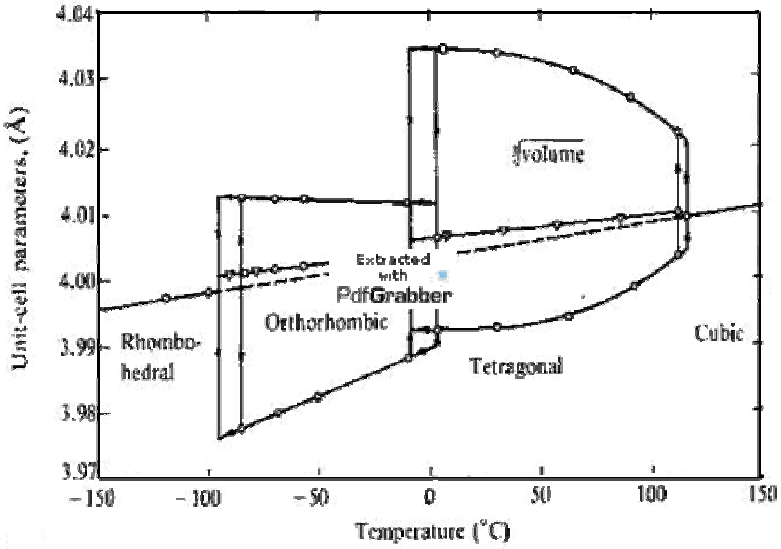



Fig 1.1 Lattice parameter $BaTiO_3$ as a function of temperature

Because the distorted octahedra are coupled together, there is a very large spontaneous polarization, giving rise to a large dielectric constant and large temperature dependence of the dielectric constant as shown in fig 1.2 .

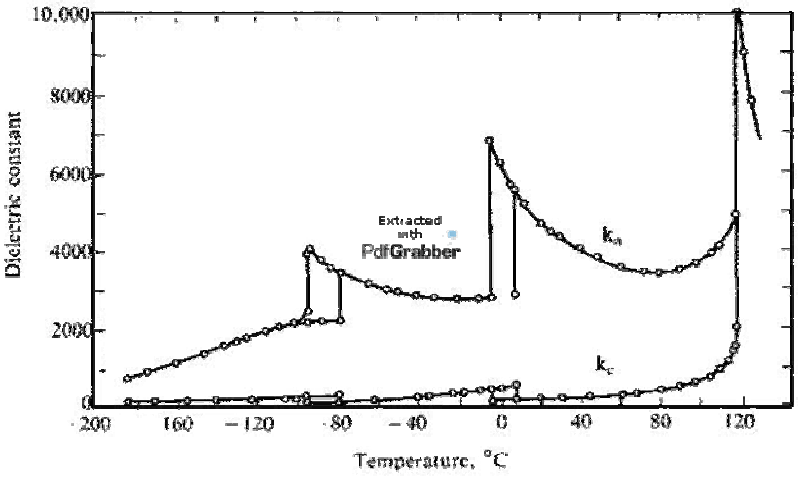



Fig 1.2 dielectric constants of $BaTiO_3$ as a function of temperature

In figure 1.1 we can see that above 120°C, Curie point Tc, barium titanate ceramic is cubic structure acting isotropic. The Ti atoms are all in equilibrium positions in the center of their octahedra. Shifting of Ti atom due to applied electric fields could cause the

structure to be altered, creating electric dipoles. For example, when temperature is below the Curie temperature, the octahedral structure changes from cubic to tetrahedral symmetry and the position of the titanium ion becomes an off-center position corresponding to a permanent electrical dipole. As the temperature is changed, the crystallographic dimensions change due to distortion of the octahedra resulting in 8 octahedra being coupled together and having a very large spontaneous polarization that leads to a large dielectric constant.

Various methods of preparation of $BaTiO_3$ is available in the literature. The solid state route needs high calcination temperature to get perovskite phase and often results in the formation of multiphase and inhomogeneous powders. High energy ball milling is also reported to produce 10nm particle size but the approach suffers from small batch size, high processing time and energy consumption. The complex double metal salts methods involve the use of solid precursors for the manufacture of pure $BaTiO_3$. The process suffers from the use of costly materials, multisteps, uncontrolled particle size and interparticle agglomeration. Pechini's autocombustion method is also reported to produce 10 nm particle size where costly materials are used but the approach suffers from small batch volume. Hydrothermal process involves the incorporation of costly materials and the optimization of it has often been a matter of empiricism. In the present paper, we report the formation of phase pure $BaTiO_3$ in the form of powders (mostly rod shaped) by a soft chemical technique where the $TiO_2$ and $Ba(NO_3)_2$ were used as starting materials, citric acid as a chelating agent and $HNO_3$ is used as an oxidizing agent.

### 1.5 Structure of $BaTiO_3$

The perovskite-like structure, named after the $CaTiO_3$ perovskite mineral, is a ternary compound of formula $ABO_3$ that A and B cations differ in size. It is considered an FCC-derivative structure in which the larger A cation and oxygen together form an FCC lattice while the smaller B cation occupies the octahedral interstitial sites in the FCC array. There is only the oxygen being B cation’s nearest neighbor. The structure is a network of

corner-linked oxygen octahedra, with the smaller cation filling the octahedral holes and the large cation filling the dodecahedral holes. The unit cell of perovskite cubic structure is shown below in Figure 1.3

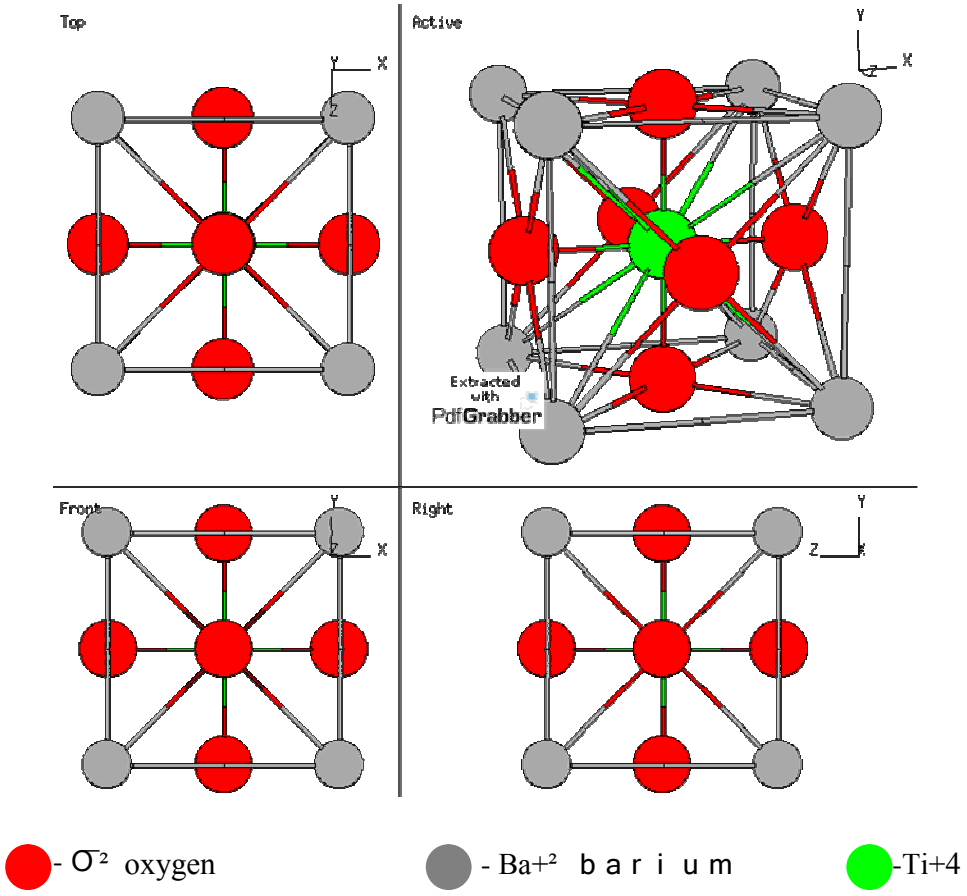



Fig 1.3 Perovskite Structure

In Figure 1.3, we can see that the coordination number of A (Ba+2 Barium) is 12, while the coordination number of B (Ti+4 Titanium) is 6. In most cases, the above figure is somewhat idealized. In fact, any structure consisting of the corner-linked oxygen octahedra with a small cation filling the octahedral hole and a large cation (if present) filling the dodecahedral hole is usually regarded as a perovskite, even if the oxygen octahedra are slightly distorted. Also, it is unnecessary that the anion is oxygen. For example, fluoride, chloride, carbide, nitride, hydride and sulfide perovskites are also classified as the perovskite structures. As a result, we can say that perovskite structure has a wide range of substitution of cations A and B, as well as the anions, but remember that the principles of substitution must maintain charge balance and keep sizes within the range for particular coordination number. Because the variation of ionic size and small displacements of atoms that lead to the distortion of the structure and the reduction of symmetry have profound effects on physical properties, perovskite structure materials play such an important role in dielectric ceramic.

### 1.6 Applications of $BaTiO_3$

Due to its PTCR properties, barium titanate is most often found used as a thermistor e.g. in thermal switches. Multilayer ceramic capacitors, due to their large capacitance, reduced volume and low cost, have become one of the fastest growing technologies in eletronic devices. Present technology uses barium titanate as the dielectric which requires the use of precious metal (Pd, Pt, Au) internal electrodes as a result of the high firing temperatures
(1300-1400C). These precious metals are responsible for 50 to 60% of the total cost of the capacitor and are subject to strategic foreign disruption. It is the goal of this investigation to evaluate the feasibility of using a polymer based dielectric and a polymer thick film metal electrode to build a multilayer capacitor that would eliminate the need for precious metals. Once this is accomplished, the next phase would ultimately involve the replacement of the silver in the polymer thick film electrode with synthetic metals. The work involved and extensive literature review, discussions with researchers active in

this field and the testing of prototype polymer capacitors. Evaluations were carried out based on capacitance, permittivity dissipation factor and short-term stability. The initial results were considered encouraging and a continuing effort in this direction is most feasible.

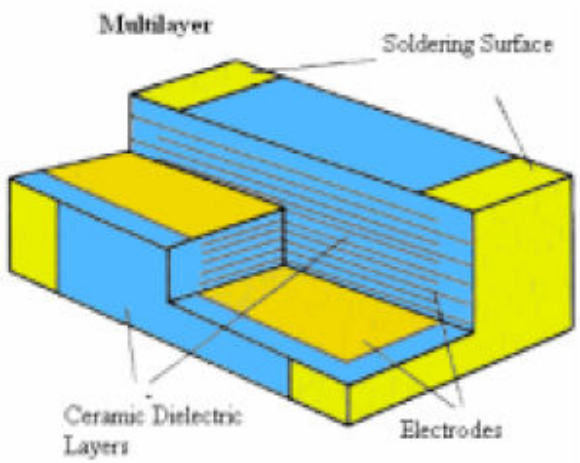



Fig – 1.4 $BaTiO_3$ Multi-layer Capacitor

# Chapter 2

## LITERATURE REVIEW

Sangjin Lee et al [1] studied the Preparation of $BaTiO_3$ nanoparticles by combustion spray pyrolysis. A 0.1 M $BaTiO_3$ precursor solution was prepared by mixing barium nitrate, $Ba(NO_3)_2$(99%, Aldrich Chem.,USA) and titanyl nitrate, $TiO(NO_3)_2$ in distilled water. $TiO(NO_3)_2$was prepared by the hydrate method starting with titanium tetrachloride, $TiCl_4$(99.9%, Aldrich Chem.) [2].Carbohydrazide, $CH_6N_4O$ (97%, Acros Organics, New Jer-sey, USA) was used as a fuel source. Ammonium nitrate, $NH_4NO_3$ (Daejung Chemicals, Korea) and ethyl alcohol(HPLC grade, Aldrich Chem.) were added to enhance thecombustion of the droplets. The stock solution for spray combustion was prepared by dissolving the precursors indistilled water with a 1:1 molar ratio of the oxidizer to the fuelfor maximum exothermic reaction [3,4]. Thermogravimet-ricanalysis (TGA) was conducted to study the thermal decomposition behavior of the precursors. Differential thermal analysis and thermogravimetric analysis (DTA/TGA) were performed to determine the optimal condition forignition. The 0.01 M stock solution was ultrasonically sprayed into a quartz tube heated at 800ºC and transported with an oxygen carrier gas flowing at 16 cm/s to maintain laminar flow conditions (Reynolds number of 1200) .

Shaohua Luo et al [5] studied the nanosized tetragonal barium titanate powders . The starting materials selected were TiCl , Ba(NO ) , citric acid and NH NO (A.R.). Citric acid was used as an organic fuel because it not only can form stable water-soluble complexes with Ti and Ba ion but is also a rich fuel [6]. Ba(NO ) compared to other barates was effective in LCS forpreparing BaTiO [7]. NH NO served as an oxidizing additive. TiO(NO ) prepared in laboratory according was chosen as the source of titanium. Herein Ba(NO ) , TiO(NO ) and NH $NO_4$3containing $NO_3$ are regarded as oxidizers, while citric acid (CA) is fuel or reducer. NH $NO_3$ were dissolved in distilled water and mixed with a TiO(NO $)_3$ solution made in laboratory. Three different Ba:Ti:CA:NH NO mixtures were prepared of the following compositions:21:1:2:8 (S1), 1:1:3:17 (S2), and 1:1:4:26 (S3). The corresponding NO:CA mixtures were: 12:2 (S1),21:3 (S2) and 30:4 (S3) . The pH value of mixture solution was adjusted to 6–7 with ammonia solution. So stable barium–titanium–citrate complexes were present and dominant in the solution without the formation of secondary phases, such as hydroxide or carbonate. This mixture solution was evaporated at | 95 8C to gradually form a clear

brown-colored resin. The resin swelled and became foamy, and was then ignited at 300 ºC at ambient atmosphere. The yellow flame rapidly spread and combustion lasted for about 2–3 min. Puffy, porous powders were obtained when the reactants were exhausted.

L. Simon-Seveyrat et al[8] studied Re-investigation of synthesis of $BaTiO_3$ by conventional solid-state reaction and oxalate coprecipitation route for piezoelectric applications $BaTiO_3$powder was prepared following the solid-state synthesis by firing at high temperature a mixture of $BaCO_3$ (Merck, 99%) and $TiO_2$(Merck, 99%). The processing steps were: ball milling for 2 h, calcining at 1150 8C for 4 h then mixing the calcined product for 3 h. The second way to make $BaTiO_3$powder was a coprecipitation process[10]: $Ti(OC_4H_9)_4$was dissolved in an aqueous solution of oxalic acid. Titanium hydroxide precipitated and reacted with oxalic acid to form soluble $TiOC_2O_4$. When the solubilisation of titanium was complete barium acetate was added slowly and a double oxalate $BaTiO(C_2O_4)_24H_2O$ was obtained .

T.V. Anuradha et al [9] studied the Combustion Synthesis of Nanostructured barium titanate Various samples of $BaTiO_3$were prepared by the solution combustion of three different barium precursors ($BaO_2$, $Ba(NO_3)_2$and $Ba(CH_3COO)_2$) and fuels such as carbohydrazide(CH), glycine(GLY) or citric acid (CA) in the presence of titanyl nitrate. In each case, titanyl nitrate was synthesized by the reaction of $TiO(OH)_2$obtained by the hydrolysis of $Ti(i\text{-}OPr)_4$with nitric acid as follows,

$$Ti{\sim}i\text{-}OC_3H_7!_41\ 3H_2O\ \ 3\ \ TiO{\sim}OH!_21\ 4C_3H_7OH$$

$$TiO{\sim}OH!_21\ 2HNO_33\ TiO{\sim}NO_3!_21\ 2H_2O$$

The stoichiometric composition of the redox mixture was calculated based on the total oxidising and reducing valency of the oxidiser and the fuel. This also serves as a numerical coefficient for the stoichiometric balance so that the equivalence ratio is equal to unity (i.e. total oxidising valency/total reducing valency (O/F) 5 1) and the energy released is maximum (7). The powders were characterized by XRD, SEM/EDAX and TEM studies besides surface area and density measurements.

The preliminary detection of phases was carried out by powder XRD using Huber diffractometer (transmission type) with a scanning speed step width of 0.01[degree] and counter time of 2 sec. Standard silicon was used as the reference

for finding the FWHM values to evaluate the crystallite sizes by Debye Scherrer's equation. SEM studies were carried out using JEOL JSM-840A microscope operating at the acceleration voltage of 20kV after coating the samples with gold. TEM images were obtained from a JEOL 2000FX-II electron microscope operating at the accelerating voltage of 200kV by depositing the methanolic suspension of the powder on carbon coated copper grids. Surface area and pore size measurements were carried out by nitrogen gas adsorption studies on the Quantachrome instrument. Powder density was measured using a pycnometer with xylene as the liquid medium.

# Chapter 3

## EXPERIMENTAL WORK

### 3.1 Introduction

Combustion synthesis, or self-propagating high temperature synthesis (SHS) provides an attractive practical alternative to the conventional methods of producing advanced materials, such as ceramics, ceramic-composites and intermetallic compounds, since SHS offers advantages with respect to process economics and process simplicity. The underlying basis of SHS relies on the ability of highly exothermic reactions to be self-sustaining and, therefore, energetically efficient. The exothermic reaction is initiated at the ignition temperature $T_{ig}$, and generates heat which is manifested in a maximum or combustion temperature, $T_c$, ***(e.g.*** 1000-6500 K), which can volatilize low boiling point impurities, and therefore result in purer products than those produced by more conventional techniques.

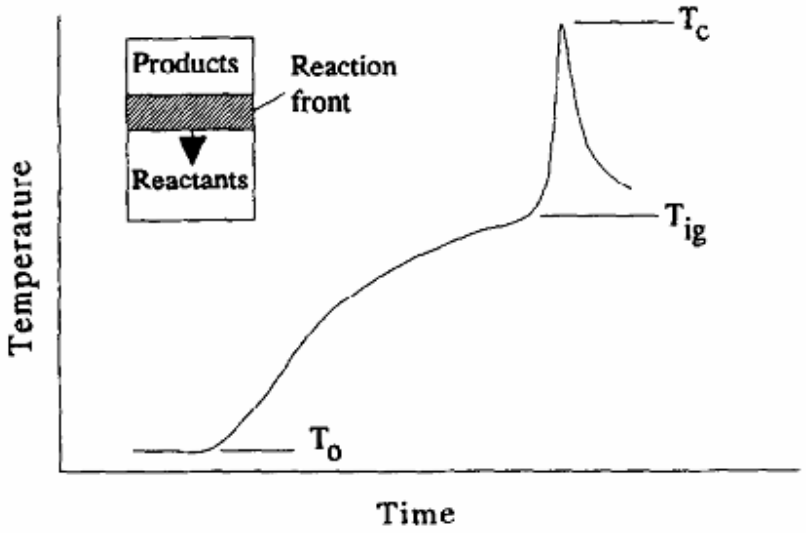



Fig – 3.1 schematic representation of the temperature time graph during an SHS reaction

In the typical combustion synthesis reaction, the mixed reactant powders are pressed into a pellet of a certain green density and subsequently ignited, either locally at one point (propagating mode) or by heating the whole pellet to the ignition temperature of the exothermic reaction (simultaneous combustion mode). A schematic representation of a typical temperature-time plot for a combustion synthesis reaction is given in Fig. 1. The products of the combustion synthesis reaction are normally extremely porous, e.g. typically 50% of theoretical density, as indicated in Fig. 2. Such porous materials may have some applications, e.g. filters and catalytic support structures, and preforms for liquid metal infiltration in the production of ceramic-metal composites. Alternatively, several techniques have been investigated as a means of densifying the SHS products, such as HIPing, hot pressing and use of shock waves.

An early application of combustion synthesis was in the 'thermite' reduction of metal oxidepowders with aluminum powder yielding either metal or an alloy of the metal and alumina.

**Advantages of Combustion Synthesis**

(1) the generation of a high reaction temperature whichcan volatilize low boiling point impurities and, therefore, result in higher purity products;

(2) the simple exothermic nature of the SHS reaction avoids the need for expensive processingfacilities and equipment;

(3) the short exothermic reaction times result in low operating andprocessing costs;

(4) the high thermal gradients and rapid cooling rates can give rise to new non-equilibrium or metastable phases;

(5) inorganic materials can be synthesized and consolidatedinto a final product in one step by utilizing the chemical energy of the reactants.

These advantages have intrigued researchers to become more active in exploring the combustion synthesis of new and improved materials with specialized mechanical, electrical, optical and chemical properties. However, there has also been some considerable research devoted to improvement of the final product quality, particularly with respect to reducing porosity.

### 3.2 Synthesis route of $BaTiO_3$

$BaTiO_3$ powders was synthesized by a soft chemical method where 0.25 M $Ba(NO_3)_2$ solution and 0.25 M $TiO(NO_3)_2$ solution, dissolved in 2 N nitric acid, were mixed together in a beaker. Tartaric acid (0.6 M) solution was then added to the resulting solution under constant stirring. The solution was then heated on a hot plate under continuous stirring condition to its boiling temperature until all the liquid evaporated. A 7 g solid ammonium nitrate was added towards the end to avoid slurry formation. There was an immense evolution of brown fumes towards the end of the reaction leaving a fluffy mass at the base of the beaker. This fine powder was dried on a hot plate at 130 °C for 30 min. The powder obtained was calcined at 900 °C for 2 h to get phase pure BaTiO3. The yield was 90%. The $TiO(NO_3)_2$ solution used for making of BaTiO3 powder was prepared in two different ways. In the first method, 1.99 g of TiO2 (AR Grade), and 10 g of ammonium sulphate (AR Grade) were added to 80 mL of concentrated H2SO4 and the mixture was stirred on a hot plate until clear solution was obtained. The formed Ti-oxysulphate was then treated with ammonia in cold condition. The precipitated TiO2·xH2O was filtered and washed free from the sulphate solution. This preciprecipitate was then treated with cold 1:1 nitric acid to get $TiO(NO_3)_2$ solution. In the second method, 8.90 g of titanium isopropoxide was first hydrolyzed with very slow addition of dilute ammonia in ice-cold condition with vigorous stirring, as the reaction was highly exothermic. The precipitated TiO2·xH2O was then filtered and washed thoroughly. This was further nitrated with the addition of 1:1 nitric acid. A change in color was observed as the white mass changed to a yellowish green transparent solution. The powders obtained by using $TiO(NO_3)_2$ prepared by the above two methods were characterized using X-ray diffraction analysis using Cu–Kα radiation. The powder morphology was studied using SEM (Leo 430i). The thermal studies (TGA and DTA) were carried out.

### 3.3 General characterization

#### 3.3.1 Thermal

Thermal decomposition of BaTiO3 powders were studied using thermogravimetric and differential scanning calorimetric (TG-DSC) by heating the sample at 10 °C/min in argon in a thermal analyzer (Model STA 4096, NETZSCH , Germany )

#### 3.3.2 X-ray diffraction

Phase analysis was studied using the room temperature powder X-ray diffraction (Model: PW 1710 diffractometer, Phillips, Netherland) with filtered 0.154056 nm Cu Kα radiation. Samples are scanned in a continuous mode from 25° – 90° with a scanning rate of 0.02 (degree) / 1 (sec).

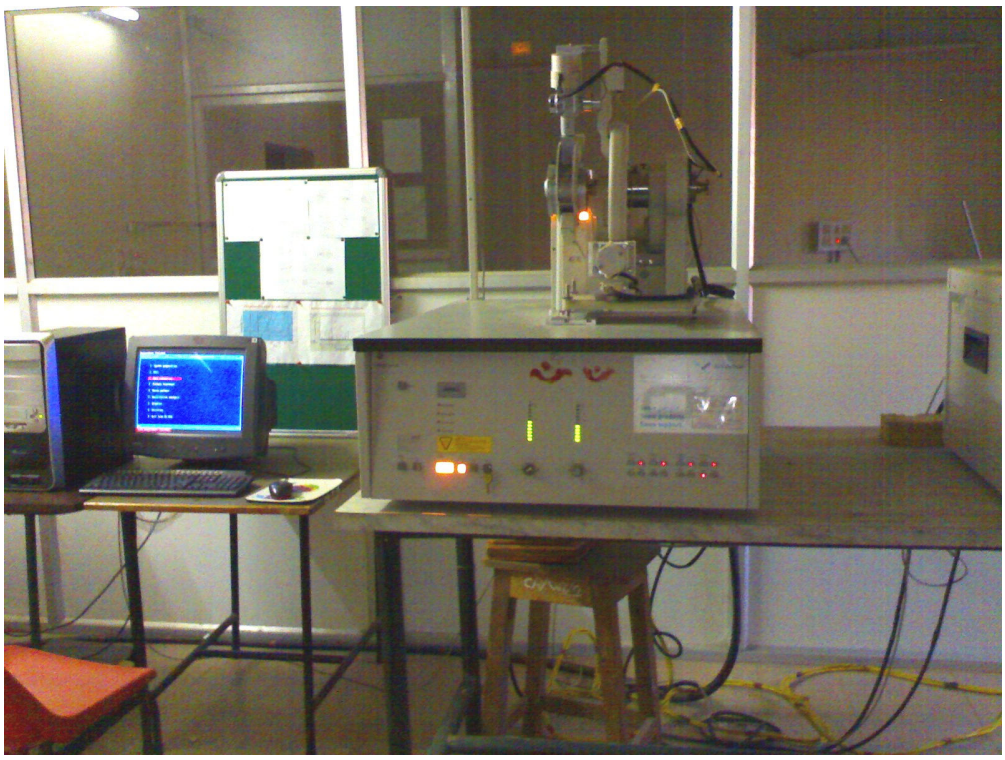
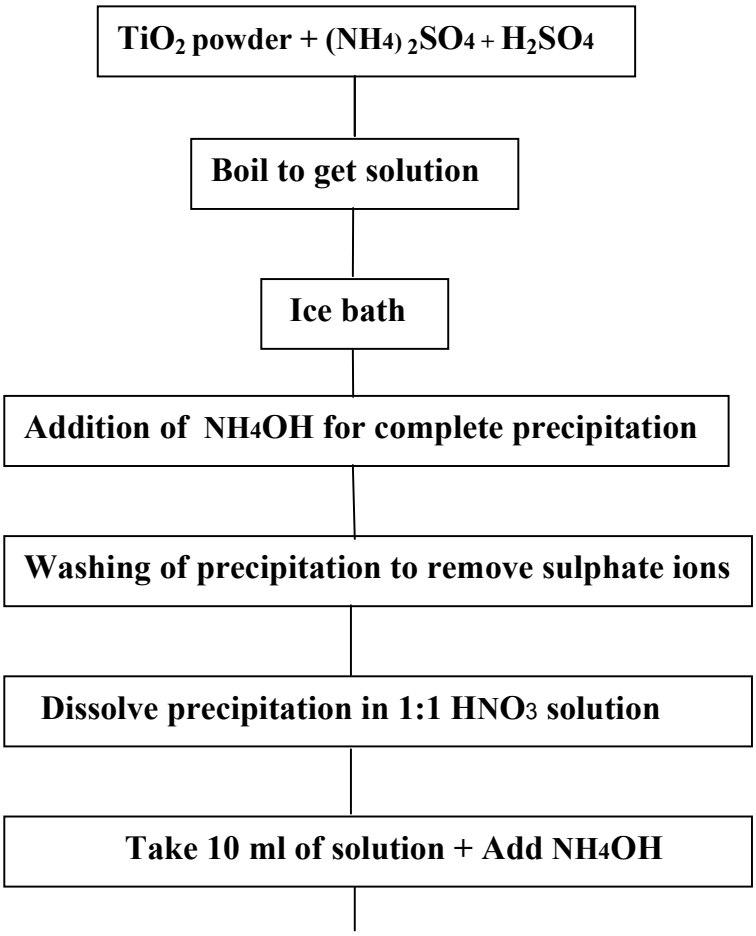


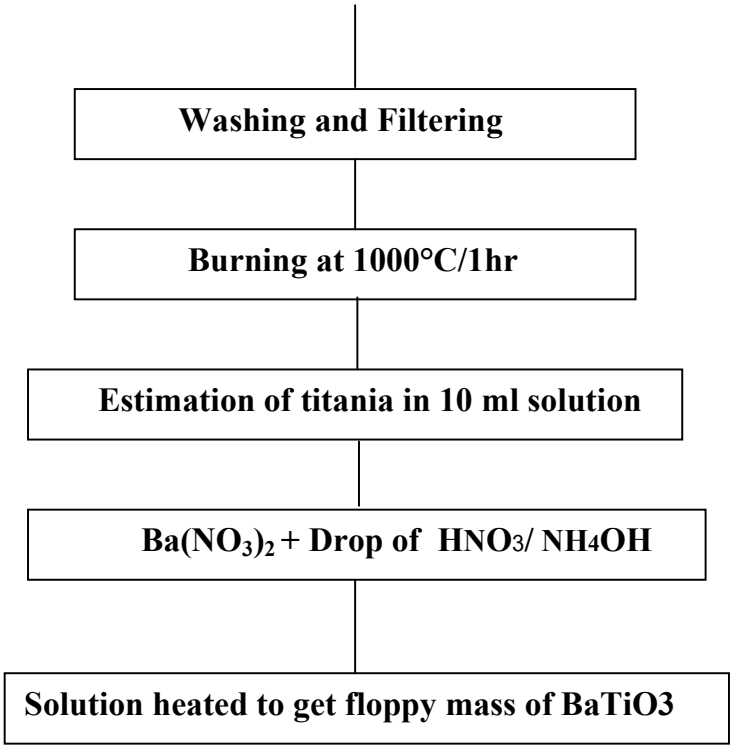
Fig – 3.2 XRD machine (Philips Analytical, Holland)

### 3.2.3 Scanning Electron Microscope

Microstructural features were studied using Scanning Electron Microscope (JSM 6480 LV JEOL, Japan). For preparation of SEM sample, the powder is dispersed in isopropyl alcohol in an ultra sonication bath (20 kHz, 500 W) for half an hour. One drop of the well-dispersed sample solution is deposited on to polished brass plate. This brass plate was used for microscopy.

## Combustion Synthesis of $BaTiO_3$ powders




Washing and Filtering
Burning at 1000°C/1hr
Estimation of titania in 10 ml solution
Ba(NO3)2 + Drop of HNO3/ NH4OH
Solution heated to get floppy mass of BaTiO3

# Chapter 4

## RESULTS AND DISCUSSION

## 4.1 Introduction

This chapter describes the thermal behavior, structure, microstructure and density of $BaTiO_3$ powder prepared through combustion synthesis technique using $Ba(NO_3)_2$ and $TiO(NO_3)_2$ solution.

## 4.2 Results and Discussion

### Thermal behavior of the $BaTiO_3$ powders

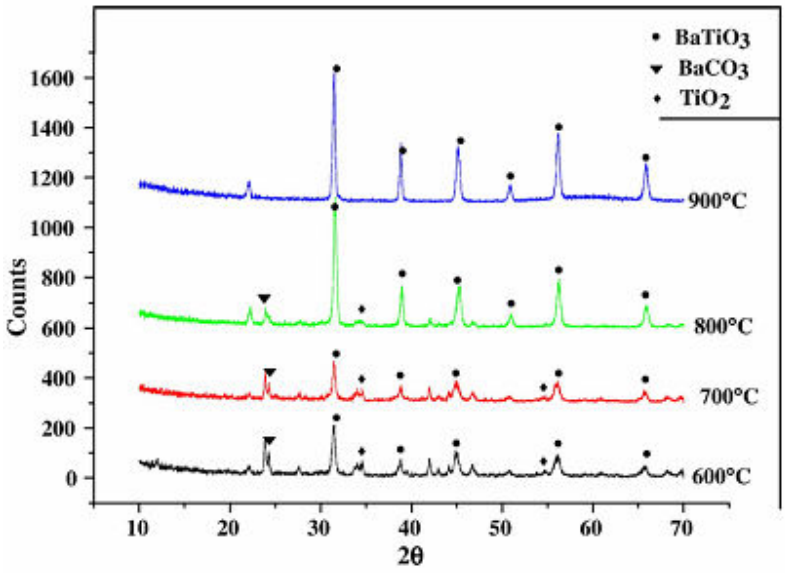



Fig – 4.1 X-ray diffraction pattern of $BaTiO_3$ calcined at 600°C , 700°C , 800°C and 900°C

Fig. 4.1 shows the XRD patterns of the synthesized powder calcined in air at different temperatures. The absence of any peak at 21.6° and 26.8° indicates that no intermediate phase like Ba2Ti2O5·CO3 is present here. Crystalline BaTiO3 is found to form at a temperature as low as 600 °C along with some impurities like BaCO3 and TiO2. As the

calcination temperature increases, the peaks become sharper and the phase pure BaTiO3 is found to form at 900 °C, which is completely devoid of any impurity phases. The average particle size, of BaTiO3 at different temperatures were calculated using

Scherrer's formula: $D = 0.9\lambda / \beta\cos\theta$

where, D is the average grain size, $\lambda$=1.541 Å (X-ray wavelength), and $\beta$ is the width of the diffraction peak at half maximum for the diffraction angle $2\theta$. The average particle size was found to be around 24 nm.

Fig. 4.2 (a). Scanning electron micrograph of powder BaTiO3 synthesized from titanium isopropoxide at 900 °C.
(b). Scanning electron micrograph of powder BaTiO3 synthesized from titanium dioxide at 900 °C.

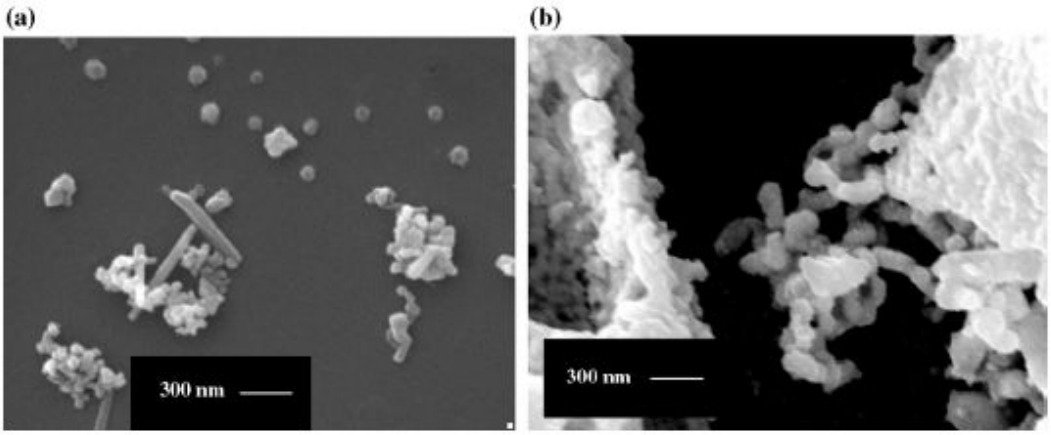



Fig. 4.2 (a) and (b) shows the micrographs of the synthesized powders formed by two different routes. The presence of considerable amount of nanorods formed by both the routes is clearly visible here. Fig. 4.3 shows the TGA curve of the synthesized powder, at a heating rate of 10 °C/min. The TGA curve depicts a loss of the weight 8.76% up to a temperature of 600 °C, which is due to the decomposition of entrapped nitrates, carboxylates, water and unburnt carbon. The weight loss at around 800 °C (5.65%) is due

to the decomposition of residual BaCO3. The corresponding DTA curve is shown in Fig. 4.4 which is in agreement with the TG analysis.

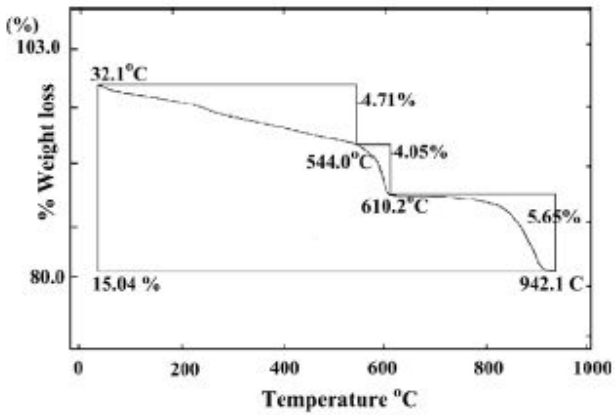



Fig. 4.3 TGA trace of BaTiO3 powder.

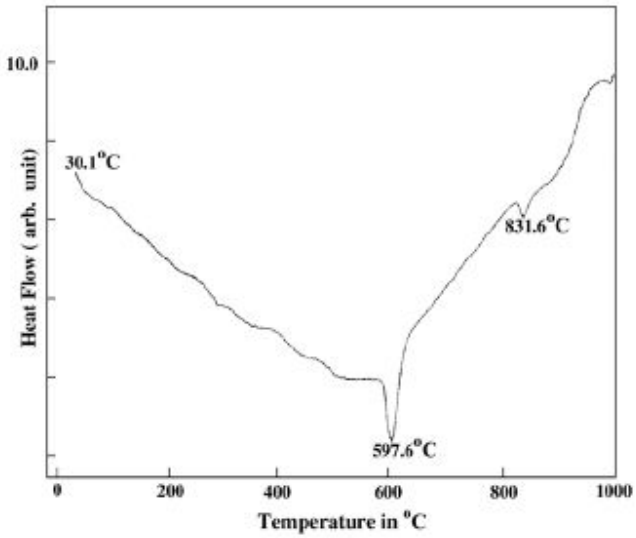



Fig. 4.4 DTA trace of BaTiO3 calcined at 800 °C

The presence of $BaCO_3$ phase is seen from the XRD trace of powders calcined at different temperatures. The absence of any $BaCO_3$ at a temperature of 900 °C in XRD shows the

completion of reaction. The presence of $TiO_2$ phase is also seen from the XRD data of powders calcined at different temperatures. The gradual decomposition of $BaCO_3$ and subsequent formation of phase pure $BaTiO_3$ is clearly seen from the XRD traces in samples calcined at different temperatures.

Different authors report the uniqueness of citric acid as a complexing agent for titanium and barium. In the present case Ba-citrate and Ti-citrate formed undergo in situ decomposition, which occurs towards the end of the reaction when nitric acid concentration is high enough to oxidize the precursors resulting in the formation of NO2, CO2 and water vapour along with discrete nanoparticles BaO and TiO2, which leads to formation of the product at a higher temperature. Small amounts of BaCO3 and TiO2 also form (as depicted from XRD) which at a higher temperature combine together resulting in the formation of phase pure BaTiO3. Synthesis of well isolated nanostructures of ferroelectric oxides have been rather scanty.

# Chapter 5

## CONCLUSIONS

The present study describes a simple low temperature combustion synthesis method of barium titanate powders . Barium titanate can be formed at a low temperature (900 °C) through citrate precursor method. Further, the oxidation of citrate precursor by $HNO_3$ was accompanied by the evolution of $CO_2$, $NO_2$ and water vapour and the gas evolution helped the product to result in a fine-grained structure.Citric acid and $HNO_3$ present in the solution play the key role for the synthesis of shaped barium titanate at a low temperature

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